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USE OF TIME-OF-FLIGHT MASS SPECTROMETRY FOR LARGE SCREENING OF ORGANIC POLLUTANTS IN SURFACE WATER AND SOILS FROM A RICE PRODUCTION AREA OF COLOMBIA

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ABSTRACT

The irrigate district of Ususaldaña, an important agricultural area of Colombia mainly devoted to rice crop production, is subjected to an intensive use of pesticides. Monitoring these compounds is necessary to know the impact of phytosanitary products in the different environmental compartments. In this work, surface water and soil samples from different sites of this area have been analyzed by applying an analytical methodology for large screening based on the use of time-of-flight mass spectrometry (TOF MS) hyphenated to liquid chromatography (LC) and gas chromatography (GC). Several pesticides were detected and unequivocally identified, such as the herbicides atrazine, diuron or clomazone. Some of their main metabolites and/or transformation products (TPs) like deethylatrazine (DEA), deisopropylatrazine (DIA) and 3,4-dichloroaniline were also identified in the samples. Among fungicides, carbendazim, azoxystrobin, propiconazole and epoxiconazole were the most frequently detected. Insecticides such as thiacloprid, or p,p'-DDT metabolites (p,p'-DDD and p,p'-DDE) were also found. Thanks to the accurate-mass full-spectrum acquisition in TOF MS it was feasible to widen the number of compounds to be investigated to other families of contaminants This allowed the detection of emerging contaminants, such as the antioxidant 3,5-di-tertbutyl-4-hydroxy-toluene (BHT), its metabolite 3,5-di-tert-butyl-4-hydroxy-benzaldehyde (BHT-CHO), or the solar filter benzophenone, among others.

KEYWORDS: Liquid chromatography, gas chromatography, TOF MS, large screening, pesticides, water, soil, rice production, pollution

INTRODUCTION

In last years, there has been an increasing concern over the presence of organic contaminants in aquatic ecosystems. This has been more evident in agricultural areas due to the frequent use of pesticides. The irrigate district Ususaldaña, Tolima (Colombia), is mainly devoted to rice production. More than 150 products are registered for use in rice production in Colombia. In addition to those pesticides applied for rice, some more pesticides are also applied for other crops existing in the area. This district uses Saldaña River as a source of water. After irrigation, it drains to streams ending up into the Magdalena River, the most important of Colombia. Magdalena river water is finally used for human consumption, being therefore necessary to monitor pesticides and other potential contaminants in soils and waters of this area.

In environmental routine analysis, monitoring is generally based on multiresidue/multiclass methodologies for target substances considered as dangerous for human health or the ecosystem. Target methods are typically focused on a limited number of priority compounds, and their main objective is the accurate quantification of target analytes. Their scope rarely exceeds several tens of analytes, being quite unusual to find analytical methods for the determination of more than 100-200 organic pollutants. The techniques most widely applied in target analysis are gas chromatography (GC) (from non-polar to semi-polar, volatile compounds) and liquid chromatography (LC) (from semi-polar to polar, non-volatile compounds) coupled to mass spectrometry (MS) using different analysers. Until recently, single quadrupole in Selected Ion Monitoring (SIM) mode has been the preferred

technique. Nowadays, triple quadrupole (QqQ) and ion trap (IT) are the predominant analyzers due to the excellent sensitivity and selectivity reached when working under tandem MS (MS/MS) **(Martínez Vidal et al. 2006) (Marín et al. 2009) (Pitarch et al. 2007) (Petrović et al. 2005; Trtić-Petrović et al. 2010; Van Nuijs et al. 2010).** Despite the strong potential of these techniques, they present a limitation in the number of compounds to be included in the scope of the method. In addition, other potentially harmful compounds might be ignored in target analysis, as only analyte-specific information is normally acquired. On the contrary, High Resolution (HR) instruments, e.g. time-of-flight (TOF), offer the possibility of investigating the presence of compounds once the analysis has been performed and MS data acquired, without being dependent on the pre-selection of analytes. An advantage of the "post-target" approach is the possibility to detect a large number of contaminants in a single analysis **(Hernández et al. 2005)(Hernández et al. 2011c).** The sensitive full spectrum acquisition and the high mass resolution and mass accuracy provided by TOF-MS make this technique especially suited for wide-scope screening in the environment, where one can find a large number and types of organic contaminants. In addition, reliable tentative identifications can be made without using reference standards. As accurate-mass full-spectrum data remain available, a retrospective analysis is also feasible at any time to investigate the presence of other compounds without additional analysis **(Hernández et al. 2011c; Ibáñez et al. 2008).**

TOF MS hyphenated to both LC or GC is playing a noticeable role for screening of organic contaminants, in relevant fields like environmental pollution **(Hernández et al. 2011a), (Ibáñez et al. 2009)(Hernández et al. 2011c; Ibáñez et al. 2008)(Díaz et al.**

2012)(Nurmi and Pellinen. 2011; Nurmi et al. 2012)(Gonzáez-Mariño et al. 2012) (Petrovic and Barceló. 2006)(Nácher-Mestre et al. 2011) (Richardson and Ternes. 2011; Richardson. 2012) or food-safety **(Ibáñez et al. 2012) (Díaz et al. 2012), (Kaufmann et al. 2007) (Cajka et al. 2008) (Ferrer et al. 2011)**. The TOF MS post-target approach has demonstrated to be an advanced tool that allows the investigation of hundreds of compounds in the same run **(Díaz et al. 2012).** The complementary application of target and non-target approaches has evident benefits in the environmental field, where many different contaminants can be present in the samples. The combined use of both approaches gives the possibility to detect non-previously selected or unexpected compounds, especially in GC methods where the availability of commercial spectral libraries simplifies this purpose **(Hernández et al. 2011c; Ibáñez et al. 2008).** However, despite the strong potential of these techniques, wide-scope screening of hundreds of compounds by combined use of GC-TOF and LC-TOF has been scarcely explored until now.

In this work, the complementary use of GC and LC coupled to TOF MS has been applied for rapid screening of a large number of organic contaminants and metabolites/TPs in water and soil samples from Ususaldaña area. As far as we know, there is not previous information on the presence of pesticides or other organic contaminants in this area.

EXPERIMENTAL

Reagents and chemicals

Reference standards of pesticides, octyl/nonyl phenols, PCBs (Mix 3, 100 µg/mL in cyclohexane; Mix 41, 10 µg/mL in cyclohexane) and PAHs (Mix 9, 100 µg/mL) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). PBDE standard mixture "Lake Michigan Study", containing BDE 28, 47, 66, 85, 99, 100, 138, 153 and 154 (50 µg/mL in isooctane) and two individual standards of BDE 71 and 183 (50 µg/mL in isooctane) were purchased from Chiron (Trondheim, Norway). When the solid reference standards were available, stock solutions (around 500 µg/mL) were prepared by dissolving reference standards in acetone and stored in a freezer at –20°C. Working solutions for GC were prepared by diluting stock solutions in acetone (quality controls preparation) or in hexane (for standards injected in the chromatographic system). For LC-MS analysis, stock solutions were diluted with acetonitrile or methanol (up to 5 mg/L) and subsequently with HPLC-grade water.

Reagent-grade sodium hydroxide, and, ultra-trace quality ethyl acetate, acetone, acetonitrile, methanol (MeOH), dichloromethane (DCM) and n-hexane were provided by Scharlab. HPLC-grade water was obtained from distilled water passed through a Milli-Q water purification system (Millipore, Bedford, MA, USA). Reagent-grade formic acid (HCOOH) (> 98%) was obtained from Fluka. Leucine enkephalin and heptacose, used as

LC-TOF and GC-TOF lock masses, respectively, were purchased from Sigma (St. Louis, MO).

500 mg Bond Elut cartridges C18 (Varian, Harbor City, CA, USA) were used for solid-phase extraction. Glass fiber filters AP 40, 47 mm x 0,7 µm size porus were from Millipore.

Sampling area under study and samples collection

Thirteen surface water samples and sediments of stream waters from the irrigate district of Ususaldaña (Tolima County, Colombia) were collected in a regional survey carried out in February 2009. Additionally, nine samples of surface soils (0-10 cm) (representative of the main soil types from the same area) were collected. The monitored streams are used for recreational and fishing activities by the population living around. **Figure 1** shows the location of sampling points. All water samples were filtered through glass fiber filters AP40 before analysis. The fresh soil samples were air-dried and ground to pass a 200 mesh sieve. Water and soil samples were maintained at -18ºC until sample preparation.

Analytical procedure

Water samples

200 mL water samples were pre-concentrated by solid-phase extraction (SPE), using 500 mg Bond Elut C18 cartridges previously conditioned with dichloromethane and methanol. Samples were percolated through the cartridges by gravity and vacuum dried for 15 min. Analytes were eluted using 5 mL of ethyl acetate:dichloromethane (1:1).

The final extract was divided in two 2.5 mL-aliquots, which were evaporated to dryness under a gentle nitrogen stream at 40ºC. The first aliquot was redissolved in 0.5 ml hexane and analyzed by GC-TOF MS. The second one was redissolved in 1 ml H_2O:MeOH (90:10 v/v) for UHPLC-QTOF MS analysis.

Soils

5 g of soil were extracted in an ultrasonic bath with 40 mL ethyl acetate for thirty minutes. Then, an extract-aliquot of 10 mL was taken, evaporated to dryness and redissolved in 1 mL of ethyl acetate. 0.4 mL aliquot was taken for direct GC-TOF MS analysis. The remaining soil extract (0.6 mL) was evaporated under a gentle nitrogen stream at 40ºC and redissolved in 1 mL H_2O:MeOH (90:10 v/v) for UHPLC-QTOF MS analysis.

Instrumentation

GC-TOF MS

An Agilent 6890N GC system (Palo Alto, CA, USA) equipped with an Agilent 7683 autosampler was coupled to a TOF MS, GCT (Waters Corporation, Milford, MA, USA), operating in electron ionization (EI) mode (70 eV). The GC separation was performed using a fused silica HP-5MS capillary column with a length of 30 m x 0.25 mm i.d. and a film thickness of 0.25 μm (J&W Scientific, Folson, CA, USA). The oven temperature was programmed as follows: 90ºC (1 min); 5ºC/min to 300ºC (2 min). Splitless injections of 1 μL sample were carried out. Helium was used as carrier gas at 1 mL/min. The interface and source temperatures were both set to 250ºC and a solvent delay of 3 minutes was selected.

The time-of-flight mass spectrometer was operated at 1 spectrum/s acquiring the mass range *m/z* 50-650 and using a multi-channel plate (MCP) voltage of 2700V. TOF-MS resolution was about 8500 at full width half maximum (FWHM) at *m/z* 614.

Heptacose, used for daily mass calibration as well as lock mass, was injected via syringe in the reference reservoir at 30ºC for this purpose. The *m/z* ion monitored was 218.9856. The application manager TargetLynx, a module of MassLynx software, was used to process the qualitative and quantitative data obtained from standards and samples for target compounds. The application manager ChromaLynx, also within MassLynx software, was used to investigate the presence of non-target compounds in samples. Library searching was performed using the commercial NIST library.

UHPLC-QTOF MS

A Waters Acquity UPLC system (Waters, Milford, MA, USA) was interfaced to a hybrid quadrupole-orthogonal acceleration-TOF MS (Q-oaTOF Premier, Waters Micromass, Manchester, UK), using an orthogonal Z-spray-electrospray (ESI) interface operating in both, positive and negative ion modes. The UHPLC separation was performed using an Acquity UPLC BEH C18 1.7 μm particle size analytical column 150 × 2.1 mm (Waters), at a flow rate of 300 μL/min. The mobile phase used was a time-programmed gradient using H_2O and MeOH, both acidified with 0.01 % formic acid. The percentage of organic modifier changed linearly from 10% to 90% in 14 minutes. The injection volume was 50 μL. Desolvation gas as well as nebulising gas was nitrogen (Praxair, Valencia, Spain). The desolvation and cone gas flow were set at 600 L/h. and 60 L/h, respectively. Collision gas

was argon 99.995% (Praxair, Valencia, Spain). TOF-MS resolution was approximately 10000 at FWHM in V-mode and 17.500 FWHM in W mode, at *m/z* 556.2771. The microchannel plate (MCP) detector potential was set to 1850 V. Capillary voltages of 3.5 and 3.0 kV were used in positive and negative ionization modes, respectively. A cone voltage of 25 V was selected. The interface temperature was set to 350ºC and the source temperature to 120ºC. The column temperature was set to 60 ºC.

For MS^E experiments, two acquisition functions were created: the low energy function (LE), selecting a collision energy of 4 eV, and the high energy (HE) function, with a collision energy ramp ranging from 15 eV to 40 eV to promote fragmentation. The LE and HE functions settings were for both a scan time of 0.2 s and an inter-scan delay of 0.05 s. The automated attenuated function (Dynamic Range Enhancement, DRE) was also selected to correct for possible peak saturations, allowing the exact mass measurement accuracy to be maintained within a wide concentration range.

Calibration experiments were monthly conducted from *m/z* 50 to 1000 with 0.05 M NaOH: 5% HCOOH (1:1) diluted (1:25) with acetonitrile:water (80:20), at a flow rate of 10 µL/min.

For automated accurate mass measurement, the lock-spray probe was used, using as lock mass a solution of leucine enkephalin (2 µg/mL, in 50:50 acetonitrile:water) at 0.1% HCOOH pumped at 30 µL/min through the lock-spray needle. A cone voltage between 60-90 V was daily selected to obtain adequate signal intensity for this compound (~ 400-500 counts). The protonated and deprotonated molecule of leucine enkephalin at *m/z* 556.2771

and *m/z* 554.2771, were used for recalibrating the mass axis and ensuring a robust accurate mass measurement along time, in positive and negative ionisation modes respectively. It should be noted that all the exact masses shown in this work have a deviation of 0.55 mDa from the "true" value, as the calculation performed by the MassLynx software uses the mass of hydrogen instead of a proton when calculating [M+H]+ exact mass. However, because this deviation is also applied during mass axis calibration, there is not negative impact on the mass errors presented in this article. MS data were acquired in centroid mode and were processed by the ChromaLynx XS application manager (within MassLynx v 4.1; Waters Corporation).

RESULTS AND DISCUSSION

GC-TOF MS screening

GC-TOF MS was used for target screening of around 150 compounds including aromatic polycyclic hydrocarbons (PAHs), octyl/nonyl phenols, polychlorinated byphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and a notable number of pesticides, such us insecticides (organochlorines, organophosphorus, carbamates and pyretroids), herbicides (triazines and chloroacetanilides), fungicides and several metabolites (see **Table S1** for the list of contaminants included in the GC-TOF MS screening, SI). The high resolution and accurate-mass measurements of GC-TOF MS allowed to obtain narrow-window eXtracted Ion Chromatograms (nw-XIC), i.e. with mass-windows of ± 0.010 mDa, at selected characteristic *m/z* ions for every compound. The presence of at least two ions measured at their accurate mass and the compliance of retention time and intensity within specified

tolerances **(Lehotay et al. 2008)** was used for reliable identification of the compound detected in the samples. The methodological approach applied was based on a previously developed and qualitatively validated method for screening and confirmation of organic micropollutants in water **(Portolés et al. 2011).** In the present work, a mixture of reference standards in solvent (50 µg/L) was injected in every sequence of sample analysis as internal quality control, in order to test the instrumental performance and analytes retention times.

Positive findings of atrazine, desethyl-atrazine and naphthalene were found in water samples, while *p,p'*-DDD and *p,p'*-DDE were found in soils **(Table 1).** As an illustrative example, **Figure 2** shows a positive finding of the herbicide atrazine in water. In this case, we observed four characteristic ions at the expected retention time in the corresponding nw-XICs. The attainment of the three Q/q_i ratios within accepted tolerances led to the unequivocal identification of this compound. The accurate mass spectrum of the sample peak is shown together with mass errors for the four ions, which were below 1.3 mDa (commonly lower than 5 ppm). Also, chemical structures for the most abundant EI fragment ions were suggested based on the elemental compositions proposed for those ions accordingly to the accurate mass measurements given by the instrument in the target methodology applied. All structures proposed for the fragments were compatible with the chemical structure of atrazine, making the identification still more reliable.

One of the advantages of using TOF MS, derived from the accurate-mass full spectrum acquisitions, is the possibility of performing a non-target analysis without additional injection of the sample extracts. In this work, the non-target analysis was made making use of ChromaLynx XS Application Manager, which automatically detects chromatographic

peaks with a response over used-defined parameters, displays their deconvoluted mass spectra to be searched in the library, and produces a hit list with positive matches. Formulae from the library hit were submitted to elemental composition calculation and up to five ions were scored by exact mass measurement for confirmation/rejection of the finding **(Hernández et al. 2011c).** Several compounds were detected and tentatively identified in this way in water samples, like the herbicides clomazone (dimethazon), oxadiazon or butachlor, the UV filter benzophenone, the PAHs cadalene and 1,6-dimethylnaphtalene, the antioxidant BHT and its transformation product BHT-CHO, and the plastic additive N-BBSA. Regarding soil samples, the flame-retarding plasticizer trybutylphosphate, the herbicides pendimethalin and butachlor, as well as the fungicides propiconazole and chlozolinate were also detected. As an example, **Figure 3** shows a positive finding of butachlor in soil using the GC-TOF MS non-target approach. Accurate mass confirmation automatically performed by the software for four representative ions led to the confirmation of the identity of butachlor in this sample. When the reference standard was available (e.g. butachlor, benzophenone) it was feasible to confirm the identity of the compound, while in the rest the identification was tentative although highly reliable due to the abundant information obtained by using TOF MS, as Figure 3 illustrates. **Table 1** shows all the compounds identified in the water and soil samples, by GC-TOF MS using both the target and non-target approaches together with the frequency of detection.

UHPLC-QTOF MS screening

The use of hybrid QTOF MS coupled to a liquid chromatographic system, allowed us to perform MS^E experiments, highly useful for screening purposes. MS^E involves the

simultaneous acquisition of exact mass data at low collision energy (LE) and high collision energy (HE) **(Tiller et al. 2008) (Hernández et al. 2011a) (Díaz et al. 2012)**. By applying LE in the collision cell, fragmentation is minimized, and information obtained is normally related to the parent molecule. However, using HE fragmentation is promoted resulting in more abundant fragments, useful for identification purposes. With all this information, obtained in a single run, the detection and identification of the compounds is highly reliable.

All MS data obtained by this approach were processed after acquisition by means of ChromaLynx XS software and a home-made compound database **(Díaz et al. 2012)**. The "post-target" processing method applied uses a list of selected exact masses and permits a rapid and simple reviewing by cataloguing analytes, as a function of mass error. In addition, the visualization of the complete spectrum (at LE and HE) is feasible for positive findings. Retention time, mass error, and i-FIT (based on the isotopic distribution and accurate masses) of each potential positive are also shown. The compound database used in this work contained around 1,000 LC-amenable organic contaminants, mainly pesticides (around 500), but also antibiotics, pharmaceuticals, illicit drugs and a notable number of transformation products/metabolites, among others (see **Table S2, SI**).

Target analytes were mostly selected based on existing compound lists encountered in the literature for LC-MS methods applied to organic contaminants determination. Around 250 reference standards were available in our laboratory and, therefore, experimental data (retention time, in-source fragment ions and/or adduct information) were also added to database for them, and used for an easier detection and identification. The identification

was favoured by the use of narrow mass windows (nw) of 0.02 Da (± 0.010 Da), and was based on mass accuracy (typically bellow 2 mDa), isotope fit, as well as retention time (maximum deviation of 2.5%) and fragmentation, when available. The methodology applied in this work has been previously validated for wastewater and natural water samples for a number of around 150 selected contaminants with satisfactory results (paper in preparation). In the present work, a mixture of reference standards in solvent (50 µg/L) was injected in every sequence of sample analysis as internal quality control, in order to test the instrumental performance and analytes retention times.

After QTOF-MS screening, several compounds could be identified with reference standards, thanks to the information given by accurate mass spectra and retention times. For example, **Figure 4** shows the nw-XIC chromatograms, as well as LE and HE TOF-MS spectra, for a water sample, where atrazine and azoxystrobin were detected and identified. Notice that atrazine could be investigated by both GC-TOF and LC-TOF analysis. The highly reliable identification obtained when using the MS^E approach. The LE spectrum of atrazine shows the peak corresponding to the protonated molecule (m/z 216.1013). The HE spectrum, instead, presents fragment ions at *m/z* 174.0531, 146.0229, 132.0325, 104.0013, 96.0554 and 79.0065, characteristics of triazine herbicides. The LE spectrum for azoxystrobin presents an abundant peak at *m/z* 426.1069 corresponding to $[M+Na]^+$ adduct and an important fragment at *m/z* 372.0984. The HE spectrum shows other important fragment ions at *m/z* 344.1028 and 329.0812. In all cases, mass errors were lower than 1.5 mDa (commonly below 5 ppm).

When the reference standard was unavailable, only the theoretical mass and empirical formulae was included in the data base. Despite the absence of additional information, a tentative identification could also be performed, which is one of the most important advantages of TOF MS. This was the case of the herbicide linuron ($C_9H_{11}N_2O_2Cl_2$), detected in a soil extract (**Figure 5**). A mass error of -0.2 mDa was encountered for this compound. Moreover, an excellent i-Fit value (0.00) was obtained, matching with the isotope distribution expected for two chlorine atoms (^{37}Cl and ^{35}Cl isotopes). On the basis of the low mass errors and the presence of two chlorine atoms in the molecule, we might assume the presence of linuron in the soil sample. But additional and relevant information was obtained from the LE and HE spectra. Thus, accurate masses of fragments of the suspected analyte could be justified from its chemical structure, and supported by data reported in the literature **(Greulich and Alder. 2008).** The characteristic isotopic pattern corresponding to two chlorine atoms was also observed for the fragments at *m/z* 132, 159 and 160. For *m/z* 182 the isotopic pattern observed matched with only one Cl atom, as corresponds to the chemical structure proposed. It seems rather obvious that the compound detected was linuron, although the final unequivocal information would require the use of reference standard. In our previous works, the subsequent acquisition of reference standards allowed to confirm all tentative identifications made which supports the high degree of reliability of tentative identification by using this technique **(Hernández et al. 2011b).**

In a similar way, the herbicide clomazone (dimethazon) and the fungicides epoxiconazole and propiconazole were also detected and tentatively identified in soil and water samples

(Greulich and Alder. 2008), using this "post-target" approach, even without reference standards.

A summary of the contaminants found after UHPLC-QTOF MS screening in the soil and water samples analyzed is shown in **Table 2**. Fifteen compounds were detected and identified following the methodology described in this article. The contaminants most frequently found in water were the herbicide atrazine (detected in all the water samples analysed), its metabolite deethylatrazine (DEA) and the fungicides carbendazim and epoxiconazole. Regarding soil samples, several fungicides were frequently detected, mainly carbendazim, azoxystobin and epoxiconazole.

It is interesting to point out that detection and identification is performed by using full MS acquisition data. Therefore, data can be reprocessed at any time in the future and re-evaluated using new or modified databases to search for other interesting compounds, simply by including their empirical formulae into the database. Retrospective analysis using HR MS has allowed the identification of metabolites of pharmaceuticals and drugs of abuse metabolites without additional injection of the sample extracts. **(Hernández et al. 2011b)**.

DATA EVALUATION

The irrigate district Ususaldaña in Tolima County (Colombia) is an important agricultural area, mainly devoted to rice production, from more than 30 years ago. Although typically the rice sowing seasons are February and August, these dates are being modified due to the

climate changes produced by “El Niño” and “La Niña” phenomenons. Pesticides are normally applied along the whole year, therefore the presence of these compounds in waters and soils is likely to be non-seasonal. Around 150 products (herbicides, fungicides, insecticides…) are registered for use in rice production in Colombia **(ICA 2010).** In addition, pesticides registered for other crops are also being used in the area. Sales of fungicides and insecticides have notably increased in the last years **(Buitrago and Gómez. 2008)** thus a higher impact in the soil-water environment is predictable.

As expected from an agricultural predominant area, pesticides were the most frequently compounds detected. Among them, herbicides and fungicides were found in a higher number of samples. Regarding herbicides, atrazine was investigated by both GC-TOF and UHPLC-QTOF MS. However, the higher method sensitivity of UHPLC-QTOF MS led to a greater number of positives in comparison with GC-TOF MS. Thus, atrazine was found in all water samples analyzed, and in 25% of soils analysed by UHPLC-QTOF MS (**Table 2**). Two of the main atrazine metabolites, deisopropylatrazine (DIA) and deethylatrazine (DEA), were also found in water and soil samples illustrating the interest of including metabolites/TPs when investigating the environmental impact of pesticides.

Although analyses in this work were directed towards qualitative purposes, e.g. the most powerful feature of TOF MS, a semi-quantitative estimation could be made by injecting calibration standards in solvent in the same sample sequence. Thus, atrazine estimated concentration in some water samples reached values up to 4 µg/L. Although there is not legislation regarding atrazine levels in surface water in Colombia, this concentration

duplicates the maximum concentration allowed by European Union in continental surface waters (maximum allowable concentration of 2µg/L) **(Directive 2008/105/EC).**

Other herbicides detected in water were terbuthylazine, diuron, clomazone (dimethazon) and oxadiazon, while pendimethalin, tributhylphosphate and linuron were found in soil samples. Butachlor was detected in both matrices. In addition to DIA and DEA, other herbicide metabolite (3,4-dichloroaniline, a metabolite of diuron), was also detected in water. Several herbicides found in samples are among the most widely used in this area for rice crop protection (e.g. clomazone, oxadiazon, butachlor and pendimetalin), but it seems clear that triazine herbicides, particularly atrazine, are also widely applied.

In relation to fungicides, carbendazim and epoxiconazole were the most frequent compounds. These fungicides have been widely detected in the environment **(Belmonte Vega et al. 2005) (Wu et al. 2009).** Carbendazim was detected in all soil samples as a result of its wide use in the area. This compound also reached, by run-off, surface water samples, where it was detected in a high frequency (62%). Epoxiconazole was detected in 54% and 62% of water and soil samples, respectively. Although with less frequency, azoxystrobin was also found in water and soil. Propiconazole and chlozolinate were only detected in soil samples. The fungicides reported as used for rice crop in this area were carbendazim and azoxystrobin.

Regarding insecticides, only thiacloprid was detected in water. In several soil samples, the presence of p,p'-DDD and p,p'-DDE, metabolites of the persistent pesticide p,p'-DDT, was

observed. Although this organochlorine insecticide was highly used in the past, its use is nowadays forbidden.

In addition to pesticides, other pollutants could be identified by TOF MS. This was the case of some PAHs, from anthropogenic origin, and that can also result from burning of vegetal material to remove weeds, a practice that is frequent in the area under study. This could explain the presence of compounds, such as naphthalene (detected in 69% of water samples) -and catalogued as priority substance by the European Union-, cadalene or 1,6-dimethylnaphtalene.

Other groups of contaminants were also discovered in the samples. It is remarkable the detection of the antioxidant BHT -allowed in small percentage as food additive-, as well as its transformation product BHT-CHO. Several authors have reported the presence of these compounds in environmental waters **(Fries and Püttmann. 2002; Soliman et al. 2004; Stuart et al. 2012)**. The plasticizer N-BBSA, considered as one of the 30 organic contaminants most frequently detected in the environment **(Stuart et al. 2012)** was found in several water samples. It might proceed from plastic containers of phytosanitary products. The solar filter benzophenone was also detected. It must be noticed that pharmaceuticals were not detected in the samples, which would imply little influence from wastewater and/or low consumption of these compounds in the area in comparison with other more urbanized areas where the consumption of pharmaceuticals is notably higher with a noticeable impact in the aquatic environment **(de Jongh et al. 2012; Osorio et al. 2012).**

After this wide-scope screening, future monitoring in the area could be focused on the compounds identified in this initial step. Then, target methods, typically based on chromatography coupled to tandem mass spectrometry, could be applied for accurate and sensitive quantification of selected contaminants. Obviously, screening by TOF MS might also continue in the near future to improve the knowledge on the contaminants present in the soil-water environment, and to detect potential changes in the pollution pattern of the area. If required, retrospective analysis of other contaminants, not considered in this initial screening, might also be performed from full-acquisition accurate-mass data acquired in this work.

CONCLUSIONS

In this paper, the application of TOF MS has allowed the screening of a large number of organic contaminants in soil and water samples. Combining GC and LC, both hyphenated to TOF MS, enlarges the scope of the screening, from non-polar/volatile compounds to polar/non-volatile ones. Thus, many different contaminants, including pesticides, PAHs, persistent organic pollutants, personal care products, pharmaceuticals, etc, and a notable number of metabolites/transformation products, formed part of the list of compounds investigated. Analyses of soil and surface water from a rice production area of Colombia has allowed the detection and identification of several pesticides used in the area under study, but also some metabolites, PAHs, solar filters and plastic additives.

Using TOF MS, the detection and identification of compounds is performed after accurate-mass full-spectrum acquisition; therefore, MS data remain available and can be reprocessed

at any time to search for additional contaminants, known or unknown metabolites/TPs, or even to perform a non-target investigation of non-selected compounds.

After TOF MS screening performed in this paper, future work could be directed towards quantification of the specific contaminants identified using target methods (preferably based on GC-MS/MS and LC-MS/MS). Additional screenings would be also desirable in the near future for better knowledge of the pollution pattern in the area and to detect possible changes in the contaminants present in the soil-water environment.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1. Location of soil and water sampling points.

Water sampling points: A1 Saldaña river; A2 Chenche river upper stream; A3 Cabuyal stream; A4 Canal Las Damas; A5 Las Damas stream; A6 Chenche river – Baura; A7 Guarapo stream; A8 Madroño stream; A9 Canal Cairo; A10 Canal Socorro; A11 Las Damas stream – Damas path; A12 San Francisco stream; A13 Magdalena river.

Soil sampling points: S1 Inceptisol Ustic; S2 Inceptisol Ustic; S3 Inceptisol Fluv; S4 Inceptisol Aquic; S5 Alfisol Aquic; S6 Entisol typic; S7 Entisol tropic-Fluv; S8 Alfisol Vertic; S9 The triangle area,

Figure 2. GC-TOF MS Extracted-ion chromatograms (mass window, 0.02 Da) showing a positive finding of atrazine in surface water. Experimental EI accurate mass spectrum. Chemical structures proposed for the most abundant EI fragment ions.

Q: quantitative ion; q_i: confirmative ion; St: reference standard; W: water sample; ✓: Q/q_i ratio within tolerance limits.

Mass errors in mDa (ppm, in brackets): m/z 215.0956: 1.2 (5.5); m/z 202.0683: 0.9 (4.4); m/z 200.0717: 1.3 (6.5); 173.0475: 0.7 (4.0)

Figure 3. Positive finding of butachlor in a soil sample using the GC-TOF MS non-target approach. Accurate mass confirmation automatically performed by the software for four representative ions.

Mass errors in mDa (ppm, in brackets): m/z 176.1087: 1.2 (6.8); 160.1129: 0.3 (1.8); 146.0964: -0.6 (-4.1); 118.0660 (2.5)

Figure 4. Detection and identification of atrazine and azoxystrobin in a water sample using UHPLC-QTOF under MS^E acquisition mode. Chromatogram (left), LE spectrum (center) and HE spectrum (right).

Mass errors for atrazine in mDa (ppm, in brackets): m/z 216.1013: -0.3 (-1.4); 174.0531: 1.5 (8.6); 146.0229: -0.4 (2.7); 132.0325: 0.6 (4.5); 104.0013: -0.2 (-1.9); 96.0554: 0.8 (8.3); 79.0065: 0.2 (2.5).

Mass errors for azoxystrobin in mDa (ppm, in brackets): m/z 426.1069: 0.3 (0.7); 404.1248: 0.2 (0.5); 372.0970: -1.4 (-3.7); 344.1028: -0.7 (2.0); 329.0812: 1.2 (3.6)

Figure 5. Detection and identification of linuron in a soil sample using UHPLC-QTOF under MS^E acquisition mode. Chromatogram (left) and LE and HE spectra (right) of the sample.

Mass errors in mDa (ppm, in brackets): m/z 271.0027: 1.0 (3.7); 249.0196: -0.2 (0.8); 182.0245: -0.2 (1.1); 160.9793: -0.6 (-3.7); 159.9715: -0.6 (-3.7); 132.9605: -0.7 (5.3)

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Table 1 Summary of organic pollutants detected in water and soil samples by target and non-target (*) screening using GC-TOF MS

	Compound	Source	Freq % (n=13) (1)
WATER	Atrazine	Herbicide	31
	Deethylatrazine (DEA)	TP (2)	7
	Naphtalene	PAH	69
	Clomazone/Dimethazon (*)	Herbicide	7
	Oxadiazon (*)	Herbicide	7
	Butachlor (*)	Herbicide	14
	Cadalene (*)	PAH	38
	1,6 dimethylnaphtalene (*)	PAH	38
	Benzophenone (*)	Solar Filter	7
	3,5 –di-tert-butyl-4-hydroxy-toluene (BHT) (*)	Antioxidant	84
	3,5 –di-tert-butyl-4-hydroxybenzaldehyde (BHT-CHO) (*)	TPs BHT	38
	N-butylbenzensulfonamide (N-BBSA) (*)	Plastic additive	31
	Compound	**Source**	**Freq % (n=8)**
SOIL	pp'DDD	Insecticide TP	12
	pp'DDE	Insecticide TP	88
	Tributylphosphate (*)	Herbicide	25
	Pendimethalin (*)	Herbicide	13
	Butachlor (*)	Herbicide	25
	Propiconazole (*)	Fungicide	13
	Chlozolinate (*)	Fungicide	13

(1) Freq %: frequency of detection (%)

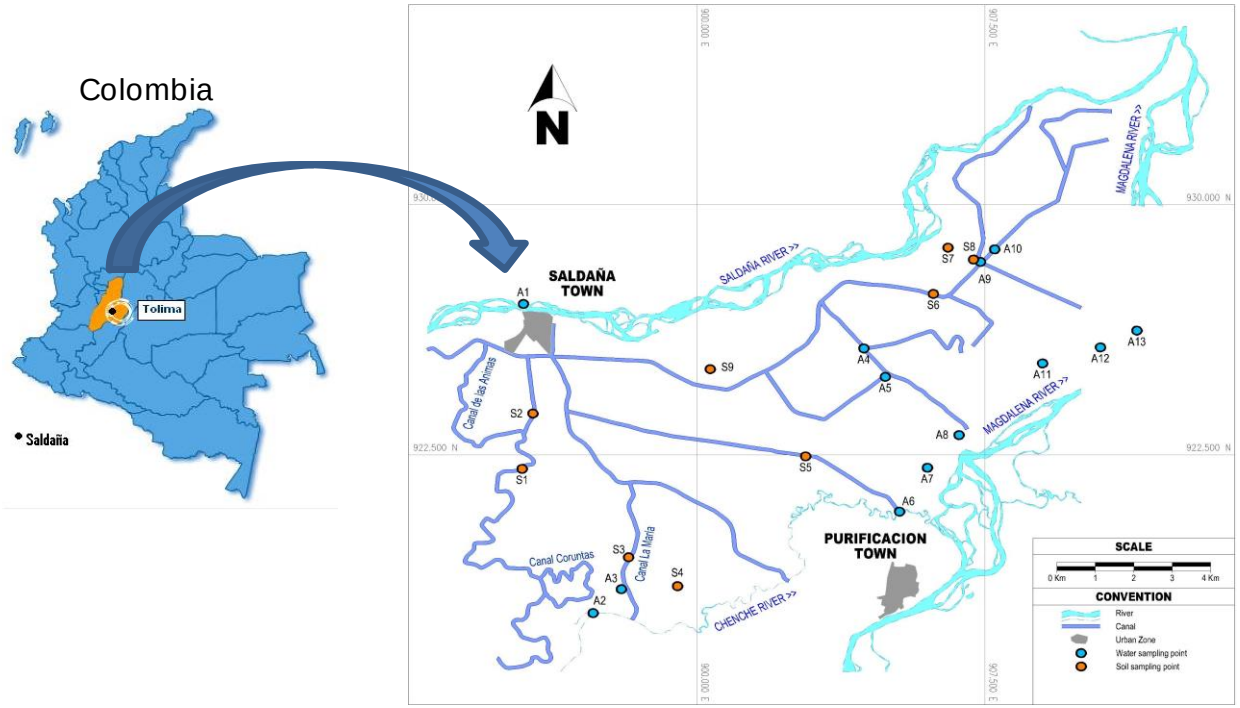
(2) TP: transformation product

Table 2 Summary organic pollutants detected in water and soil samples by target screening using UHPLC-QTOF MS

	Compound	Source	Freq % (n=13) (1)
WATER	Atrazine	Herbicide	100
	Deisopropylatrazine (DIA)	Atrazine TP (2)	8
	Deethyl-atrazine (DEA)	Atrazine TP	46
	Terbuthylazine	Herbicide	7
	Clomazone/Dimethazon	Herbicide	31
	Diuron	Herbicide	8
	3,4-dichloroaniline	Diuron TP	8
	Azoxystrobin	Fungicide	8
	Carbendazim	Fungicide	62
	Epoxiconazole	Fungicide	54
	Propiconazole	Fungicide	21
	Thiacloprid	Insecticide	23
	Compound	**Source**	**Freq % (n=8)**
SOIL	Atrazine	Herbicide	25
	Deisopropylatrazine (DIA)	Atrazine TP	13
	Deethyl-atrazine (DEA)	Atrazine TP	13
	Linuron	Herbicide	13
	Carbendazim	Fungicide	100
	Azoxystrobin	Fungicide	63
	Clomazone/Dimethazon	Fungicide	13
	Epoxiconazole	Fungicide	62
	Propiconazole	Fungicide	38
	Dichlorophenol	TP	25

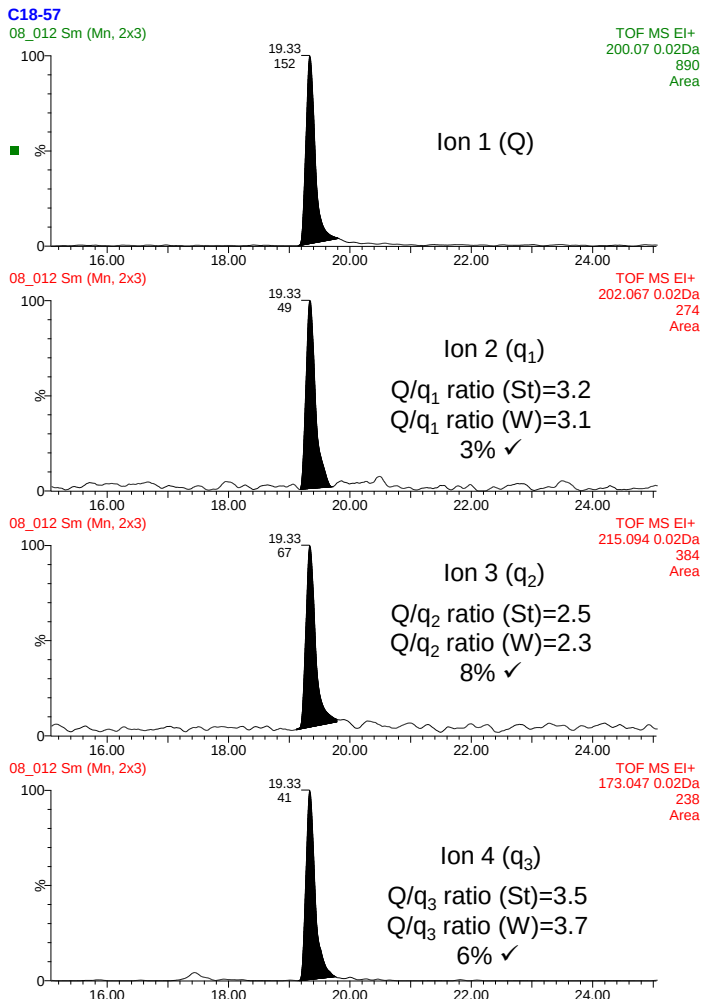
(1) Freq %: frequency of detection (%)

(2) TP: transformation product



Main Agriculture activities: RICE, CORN, COTTON and SORGHUM

Figure 1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Area
19.33
152
Ion 1 (Q)
08_012 Sm (Mn, 2x3)
TOF MS EI+
202.067 0.02Da
274
Area
19.33
49
Ion 2 (q1)
Q/q1 ratio (St)=3.2
Q/q1 ratio (W)=3.1
3% ✓
08_012 Sm (Mn, 2x3)
TOF MS EI+
215.094 0.02Da
384
Area
19.33
67
Ion 3 (q2)
Q/q2 ratio (St)=2.5
Q/q2 ratio (W)=2.3
8% ✓
08_012 Sm (Mn, 2x3)
TOF MS EI+
173.047 0.02Da
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Area
19.33
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Ion 4 (q3)
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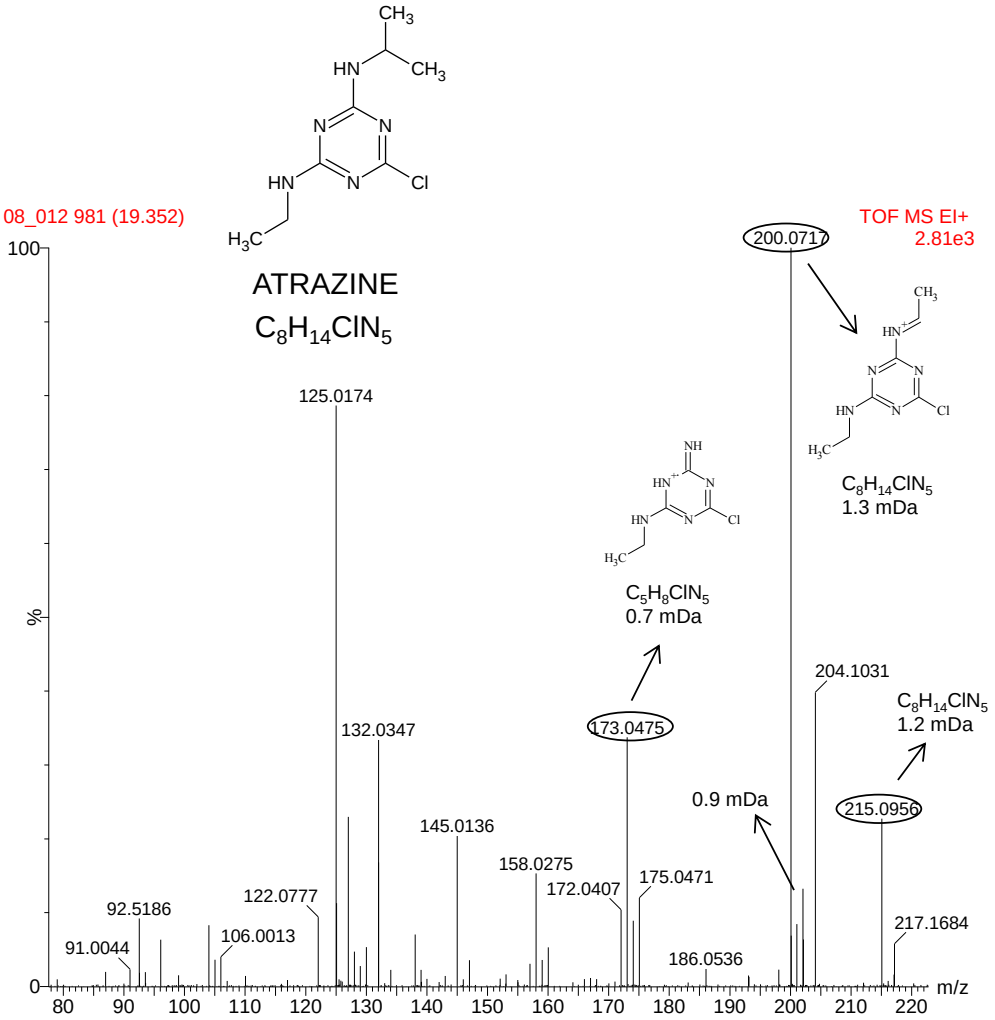
18.00
20.00
22.00
24.00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132.0347
204.1031
C8H14ClN5
1.2 mDa
C8H14ClN5
1.3 mDa
C5H8ClN5
0.7 mDa
173.0475
0.9 mDa
215.0956
145.0136
158.0275
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91.0044
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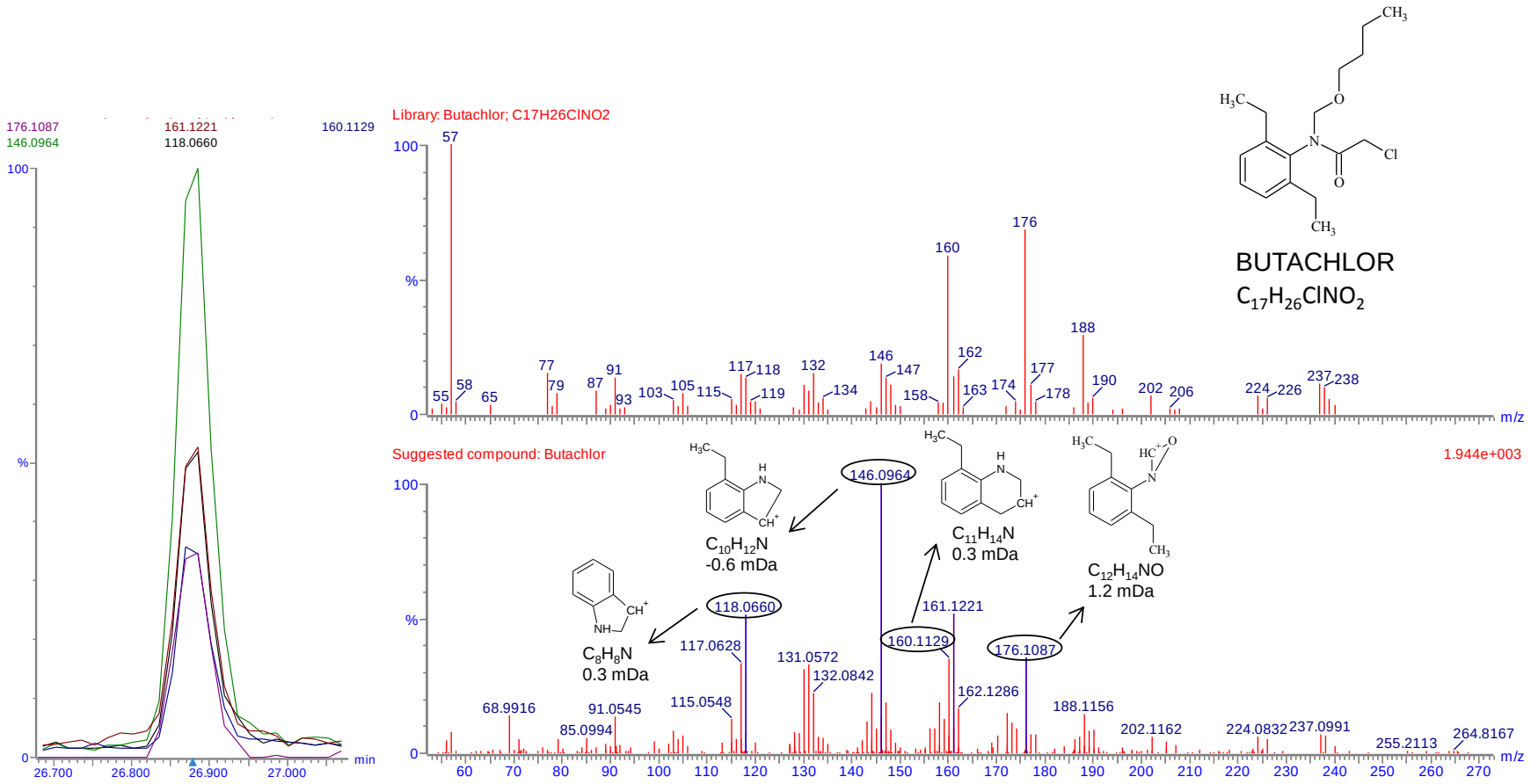
217.1684
m/z

Figure 2


176.1087
146.0964
161.1221
118.0660
160.1129
Library: Butachlor; C17H26ClNO2
BUTACHLOR
C17H26ClNO2
Suggested compound: Butachlor
1.944e+003
C10H12N
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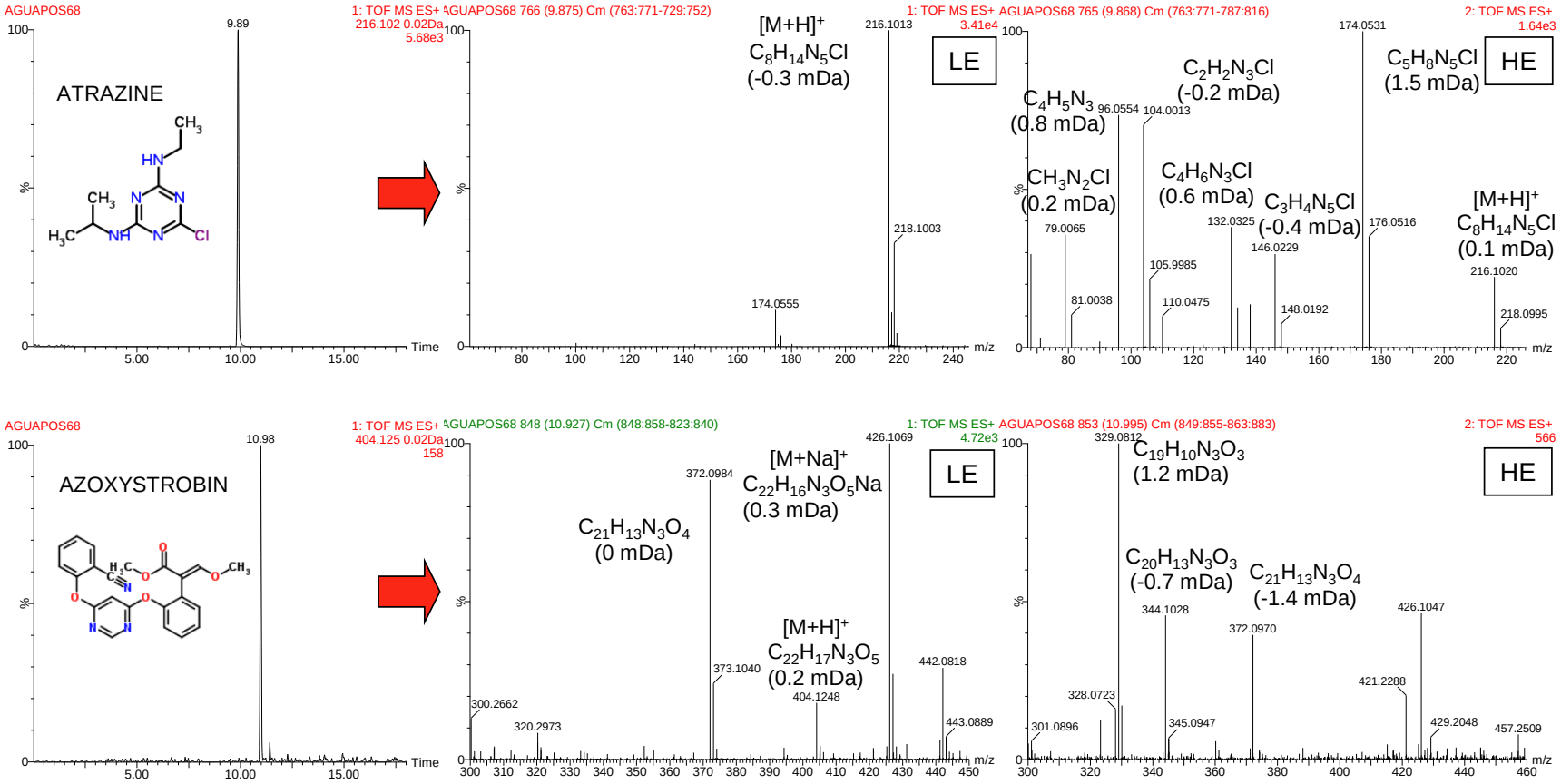
0.3 mDa
C12H14NO
1.2 mDa
C8H8N
0.3 mDa
m/z
min

Figure 3


AGUAPOS68
ATRAZINE
9.89
Time
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5.68e3
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C8H14N5Cl
(-0.3 mDa)
LE
216.1013
218.1003
174.0555
m/z
1: TOF MS ES+ AGUAPOS68 765 (9.868) Cm (763:771-787:816)
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C4H5N3
(0.8 mDa)
96.0554
104.0013
C2H2N3Cl
(-0.2 mDa)
CH3N2Cl
(0.2 mDa)
C4H6N3Cl
(0.6 mDa)
C3H4N5Cl
(-0.4 mDa)
132.0325
146.0229
105.9985
79.0065
81.0038
110.0475
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HE
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(0.1 mDa)
216.1020
218.0995
AGUAPOS68
AZOXYSTROBIN
10.98
Time
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158
426.1069
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(0.3 mDa)
LE
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C21H13N3O4
(0 mDa)
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C22H17N3O5
(0.2 mDa)
373.1040
442.0818
404.1248
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320.2973
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m/z
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329.0812
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(-0.7 mDa)
C21H13N3O4
(-1.4 mDa)
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426.1047
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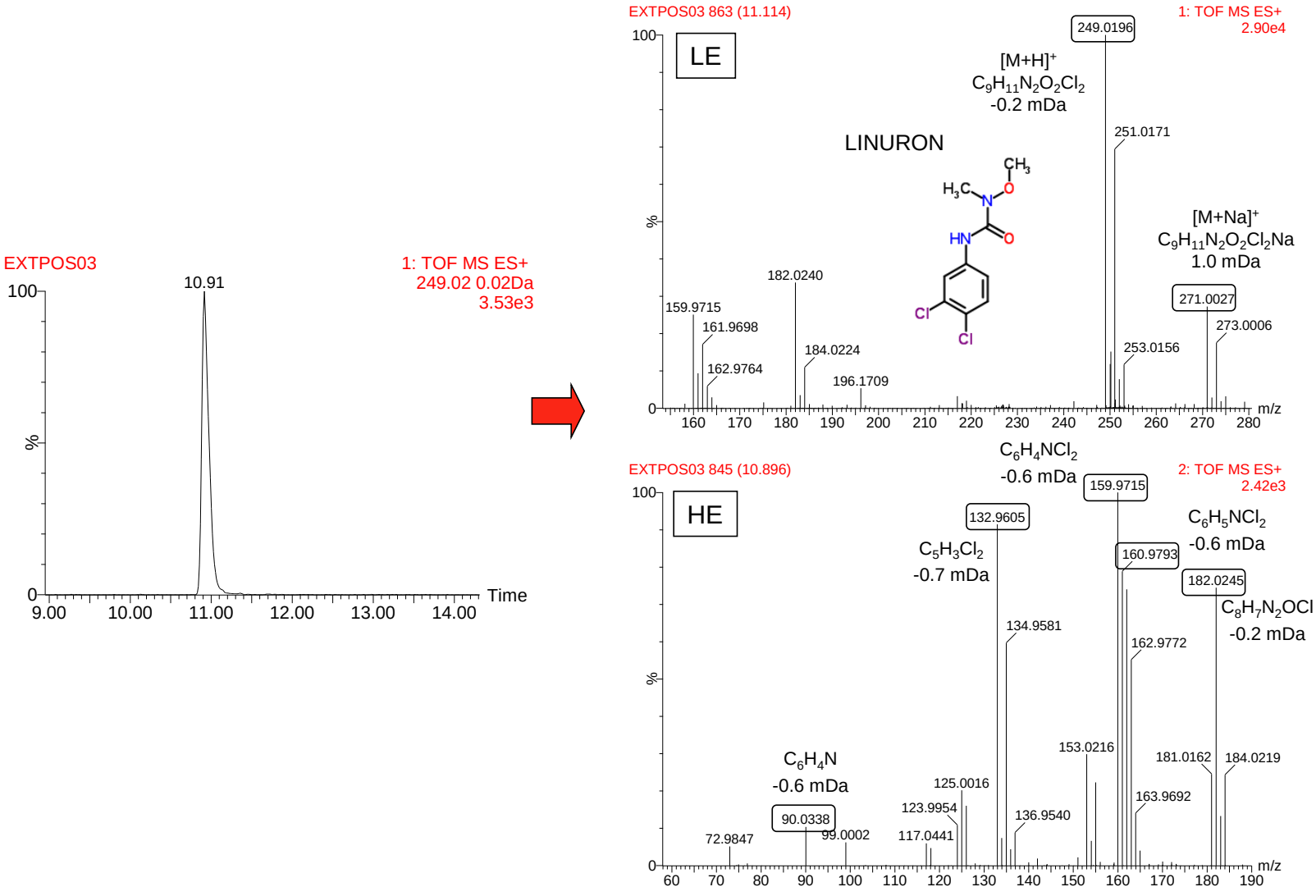
2: TOF MS ES+
566
HE
m/z

Figure 4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%
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9.00
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Time
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m/z
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Figure 5